

Optical Properties of TiO₂ Doped ZnO-PVA Nanocomposites

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Abstract. One of the materials with the greatest potential for use in flexible devices is semiconductor nanocomposite material. In this paper, we report the synthesis of ZnO-PVA-TiO₂ nanocomposite to be applied as a flexible optical sensor device. The optical property of ZnO-PVA nanocomposite is improved by the addition of TiO₂ in this work. The optical characteristics of the ZnO-PVA nanocomposite depend on the concentration of TiO₂. Spin coating method was successfully used to synthesize ZnO-PVA-TiO₂ with various TiO₂ concentrations of 1%, 2%, and 3% w/v, respectively. The absorbance spectrum of ZnO-PVA-TiO₂ nanocomposite changes with the addition of TiO₂. The absorbance peaks of ZnO-PVA-TiO₂ nanocomposites were shifting to a lower wavelength, resulting in increasing the nanocomposite band gap energy. According to this result, future applications of the flexible optical sensor are one of the potential devices based on this study.

1. Introduction

Nanocomposite materials have succeeded in revolutionizing the world with their higher impacts and wider functions. Nanocomposite materials are currently used in general automotive and industrial applications, such as the construction of biosensors for both biological, chemical, and environmental monitoring [1]. With a small size of nanometers, nanocomposites show rare properties, one of which is the increased phase relationship in the bonds [2]. Based on the type of matrix material used, nanocomposites are classified into three, namely ceramic material matrix (CMNC), metal matrix nanocomposite (MMNC), and polymer matrix nanocomposite (PMNC) [3]. PMNC-type nanocomposites show considerable improvement based on different properties such as mechanical, optical, thermal stability, and chemical resistance. Polymer-based nanocomposites are advantageous for energy harvesting and storage devices, flexible appearance, and implantable bioelectronics due to their great flexibility, high surface area, lightweight, and porous architectures [4],[5].

In this study, a polymer matrix was used in the form of conductive polymer polyvinyl alcohol (PVA) and nanoparticles served as filler in the form of metal oxide. PVA is a polymer that is semi-crystalline, soluble in water, non-toxic, and has the ability to form uniform layers. In addition, PVA is an efficient polymer for the development of OLED applications, solar cells, sensors, and optoelectronics [6–8]. ZnO is used as a filler since its potential applied in optoelectronic applications has attracted attention with a

wide band gap E_g (at 300K) = 3.4 eV with a relatively short wavelength region, a relatively large exciton binding energy of 60 meV, and semiconductors in groups II–VI that crystallize in cubic or hexagonal/wurtzite structures. In the case of ZnO, most of it is in the form of wurtzite crystals [9]. Besides that, the use of ZnO as a filler in ZnO-PVA nanocomposites is due to its non-toxic nature, chemical stability, and strong luminescent material, as well as improving the performance of PVA. Until now, it has been quite rare to find reports about the doping of certain metals to ZnO-PVA nanocomposites, especially TiO₂. The use of TiO₂ as a dopant for ZnO-PVA nanocomposites is due to its extreme stability, high refractive index, super optical transmittance, low cost, large energy band gap of around 3.2 eV, which is also used as an absorber for ultraviolet radiation, and weak toxicity. TiO₂ in the anatase phase shows an increase in absorbance and optical conductivity characteristics while the energy gap decreases [10]. Therefore, this research wanted to know the effect of the addition of TiO₂ on the optical properties of ZnO-PVA nanocomposites. The ability of TiO₂ to absorb ultraviolet light, enables the nanocomposite, to produce reducing and oxidizing compounds on the polymer surface. The addition of TiO₂ can improve the performance of ZnO-PVA nanocomposites when used as optical sensors.

2. Material and Methods

Materials used in this study polyvinyl alcohol (PVA, 87 – 90% hydrolyzed), Zinc oxide nanopowder (ZnO, <100nm particle size), and Titanium dioxide (TiO₂, <100nm particle size) were obtained from Sigma-Aldrich. All the materials were used without further purification.

2.1. Synthesis of the ZnO-PVA thin film nanocomposite

To prepare the ZnO-PVA nanocomposite, 0.75 grams of PVA were dissolved in 5 ml of distilled water to form a PVA solution. The mixture solution was then stirred at 45°C for 2 hours until a transparent solution was obtained, and then 0.15 gram of ZnO nanopowder was added to the PVA solution and mixed for 2 hours. To obtain a homogeneous and dispersed solution, sonication was carried out for 30 minutes. Next, proceed with the spin coating technique by dripping 100 μ L of the solution onto a glass substrate to get a thin film. The glass substrate was set to rotate at a speed of 1000 rpm for 20 seconds. The thin layer of film was then annealed at 50°C for 45 minutes.

2.2. Synthesis of the ZnO-PVA thin film nanocomposite with TiO₂ addition

To prepare the ZnO-PVA-TiO₂ nanocomposite, 0.75 grams of PVA were dissolved in 5 ml of distilled water to form a PVA solution. The mixture solution was then stirred at 45°C for 2 hours until a transparent solution was obtained, and then 0.15 grams of ZnO nanopowder was added to the PVA solution, followed by the additions of TiO₂ nanopowder at various concentrations of 1%, 2%, and 3% w/v to be mixed for 2 hours. To obtain a homogeneous and dispersed solution, sonication was carried out for 30 minutes. The next process was the spin coating technique by dripping 100 μ L of the solution onto a glass substrate to get a thin layer film. The glass substrate was set to rotate at a speed of 1000 rpm for 20 seconds. The thin film was then annealed at 50°C for 45 minutes.

2.3. Characterization of the synthesized ZnO-PVA nanocomposite

The characterization of the ZnO-PVA and ZnO-PVA-TiO₂ nanocomposites was carried out using a (i) JEOL JSM IT300/OXFORD XMAX 20 instrument for Scanning electron microscope (SEM)/Energy-dispersive X-ray Spectroscopy (EDX) test with a beam energy of 20kV and a magnification of 500x to 30kx to analyze the morphology of the material surface; (ii) an X-ray diffractometer (Bruker D8 Advance 3kW XRD tool) for X-ray diffraction (XRD) characterization with LynxEye XE-T detector and Cu K α radiation source ($\lambda = 1,54060 \text{ \AA}$) at room temperature 23°C with 50% humidity to analyze the crystallinity and the XRD pattern of the materials; (iii) a Shimadzu UV-1800 UV-Vis Spectrophotometer to analyse the optical properties of the materials.

3. Result and Discussion

3.1. SEM-EDX Analysis

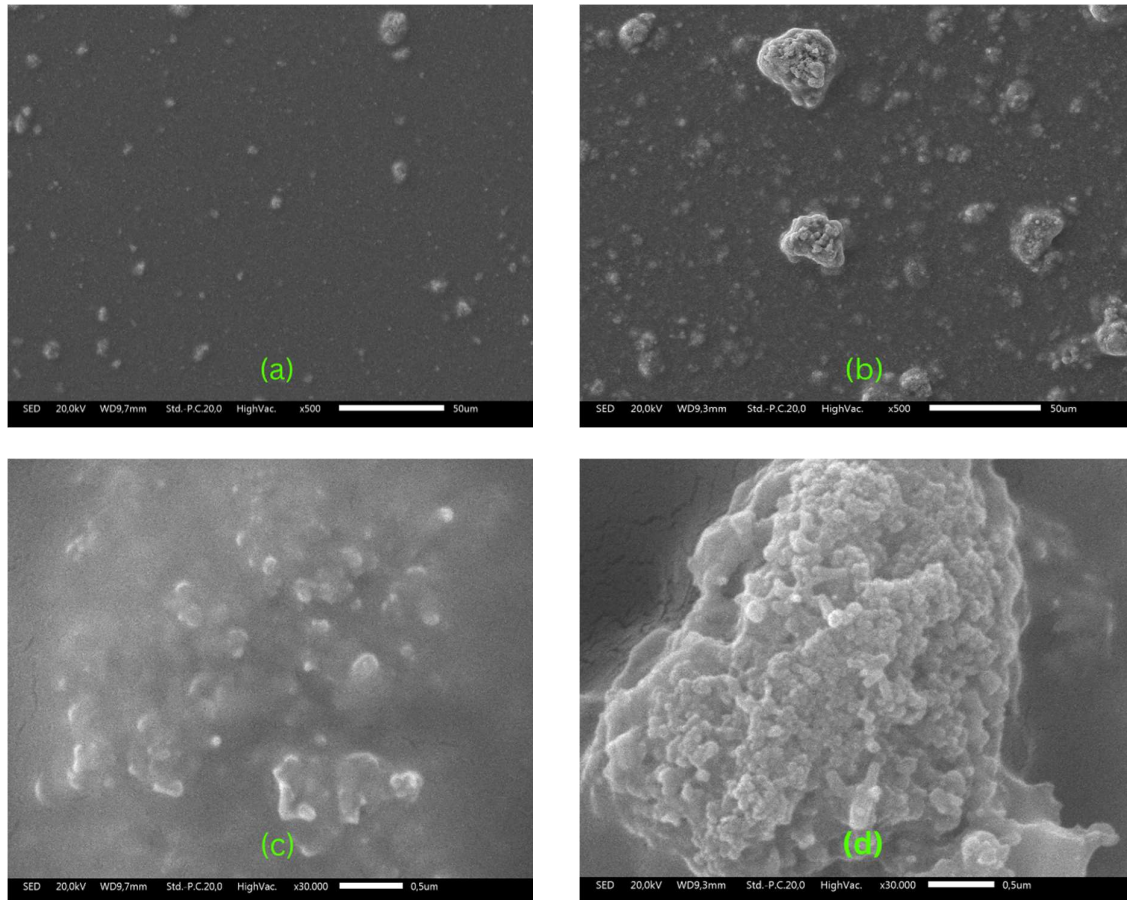


Figure 1. SEM image shows the surface of thin layer film of (a) ZnO-PVA and (b) ZnO-PVA-TiO₂ at a scale of x 500x. Then, Figure (c) and (d) show the surface thin film at a scale of 30,000x

Figure 1(a) and 1(b) show the morphology of the Scanning Electron Microscope (SEM) images of the surface thin film of ZnO-PVA and ZnO-PVA-TiO₂, respectively. The SEM image observed in Figure 1(a) shows that the ZnO-PVA nanocomposite has a smoother surface thin film than the ZnO-PVA-TiO₂ nanocomposite in Figure 1(b). It is observed that the ZnO nanoparticles are distributed throughout the polymer matrix, thus making the ZnO nanoparticles form small aggregates when homogeneously dispersed in the PVA polymer matrix [11]. This is as shown in Figure 1(c) which appears more uniform. The image in Figure 1(b) shows a difference in the surface, it is clearly seen when ZnO-PVA is added with TiO₂ the surface appears rougher and less ordered. In this case, it is due to the defects from the additional content in the PVA nanoparticles [12], thus a large number of TiO₂ appears to have agglomerated on the ZnO-PVA as seen in Figure 1(d). Figure 2(b) and (d) show the spectra of the respective Energy Dispersive X-Ray Analysis (EDX) of the thin film of ZnO-PVA and ZnO-PVA-TiO₂, respectively. The presence of the main elements zinc (Zn) and titanium (Ti) were found by the elemental content analysis of the nanocomposites ZnO-PVA and ZnO-PVA-TiO₂ as it is shown in Figure 2(b) and 2(d). Ti was observed due to the presence of TiO₂. In addition, carbon (C) and oxygen (O) was found due to the presence of the PVA nanoparticles. Meanwhile, sodium (Na), silicon (Si), and calcium (Ca)

were found in the nanocomposite due to the use of the glass substrate and the resulting process of annealing[13]. The EDX spectra show the atomic and weight percentages of the elemental content present in the thin film of the ZnO-PVA and ZnO-PVA-TiO₂ nanocomposites, it is shown in Table 1.

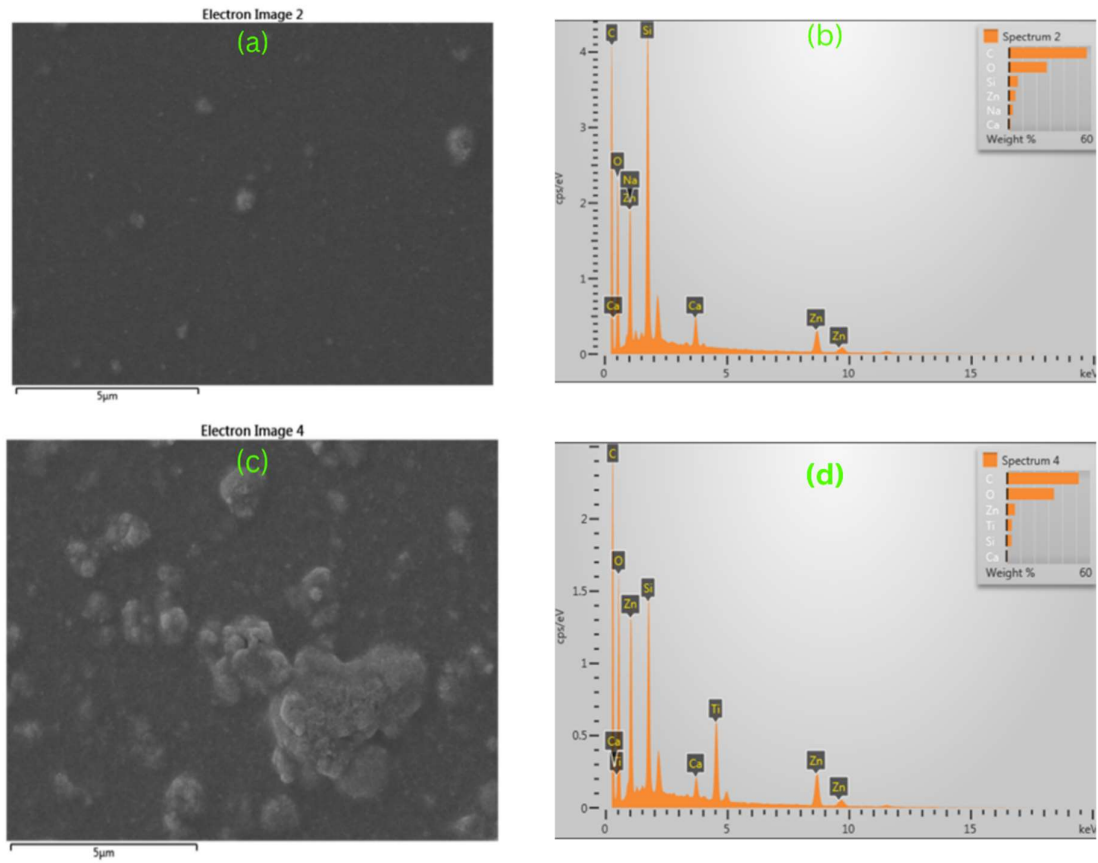


Figure 2. (a,b) A thin film of ZnO-PVA and the elemental composition from EDX on ZnO-PVA. (c,d) A thin film of nanocomposite ZnO-PVA-TiO₂ and the elemental composition from EDX on ZnO-PVA-TiO₂.

Table 1. Analysis of the Components Related to ZnO-PVA and ZnO-PVA-TiO₂ Nanocomposites

Nanocomposite	Element	Atomic %	Wt%
ZnO-PVA	Carbon (C)	68.29	56.80
	Oxygen (O)	24.92	27.61
	Natrium (Na)	1.90	3.03
	Sillicon (Si)	3.43	6.68
	Calcium (Ca)	0.40	1.12
	Zinc (Zn)	1.05	4.76
ZnO-PVA-TiO ₂	Carbon (C)	63.81	51.82
	Oxygen (O)	31.54	34.12
	Sillicon (Si)	1.86	3.54
	Calcium (Ca)	0.25	0.67
	Titanium (Ti)	1.18	3.82
	Zinc (Zn)	1.36	6.03

3.2. XRD Analysis

The XRD patterns of the ZnO-PVA and ZnO-PVA-TiO₂ nanocomposites are shown in Figure 3. The XRD pattern of the thin film ZnO-PVA nanocomposite shows three major peaks at $2\theta = 31.835^\circ$, 34.491° , and 36.322° , indicating that ZnO has a hexagonal wurtzite structure and a crystalline phase (JCPDS No. 36-1451). Meanwhile, the XRD pattern of the thin film ZnO-PVA-TiO₂ nanocomposite shows an increase in intensity peaks at $2\theta = 25.379^\circ$ and 27.433° , indicating the presence of TiO₂ with a mixed anatase and rutile phase (JCPDS No. 88-1175 and JCPDS No. 84-1286) and three major peaks at $2\theta = 31.793^\circ$, 34.468° , and 36.295° , therefore the addition of TiO₂ nanoparticles does not have a major effect on the crystalline structure of ZnO, but the addition of TiO₂ nanoparticles in the ZnO-PVA nanocomposite can affect the decrease in the 2θ peak intensity. The average crystallite size for ZnO and TiO₂ inorganic nanoparticles was measured through the Debye Scherer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where 0.9 is the Scherrer constant, λ is the X-ray wavelength (1.54060 Å), β is the FWHM, and θ is the diffraction angle. The average crystallite size of ZnO and TiO₂ nanoparticles is in accordance with the index of the surface, with the result of ZnO nanoparticles at three major peaks is 27.839 nm and TiO₂ nanoparticles is 20.731 nm for the anatase phase at $2\theta = 25.379^\circ$ and 40.624 nm for the rutile phase at $2\theta = 27.433^\circ$. The addition of TiO₂ nanoparticles also affects the average crystallite size of the ZnO-PVA nanocomposite, where before the addition of TiO₂, the average crystallite size was 31.012 nm, becoming 30.087 nm after the addition of TiO₂ [14].

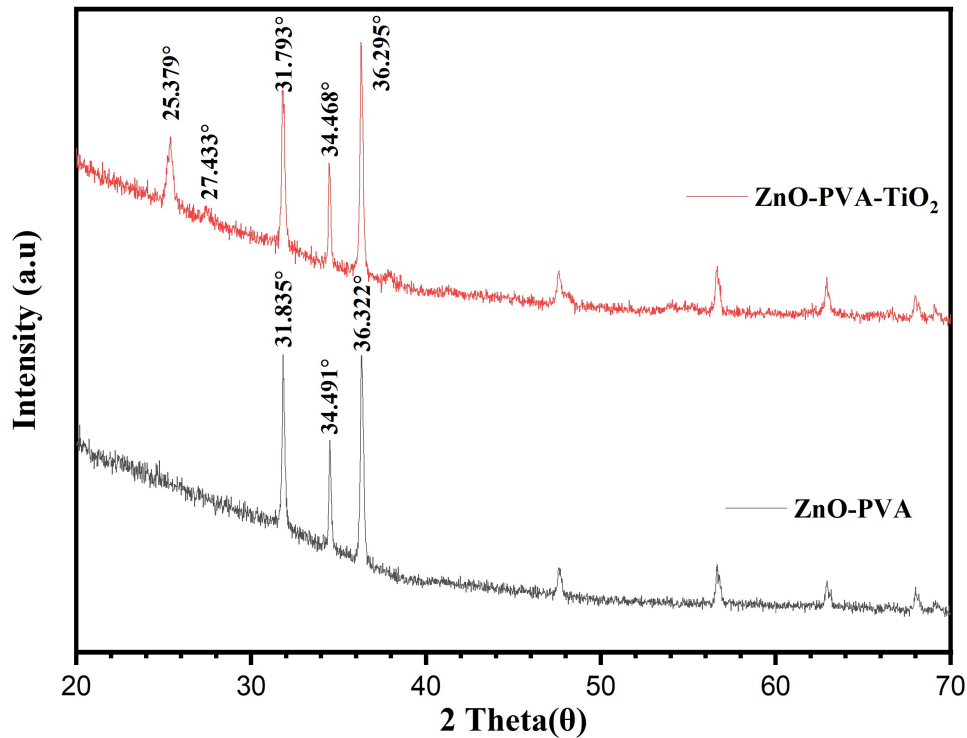


Figure 3. XRD patterns of ZnO-PVA and ZnO-PVA-TiO₂ nanocomposite thin films

3.3 UV-Vis Absorption

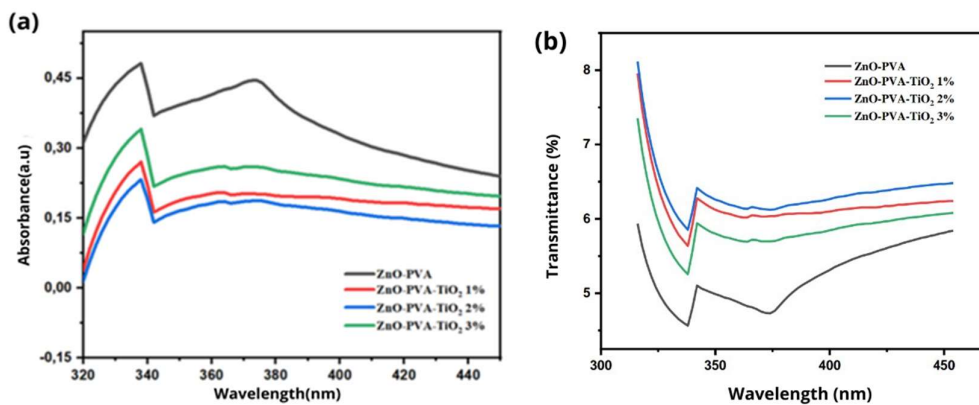


Figure 4. (a) Absorbance spectrum (b) Transmittance Spectrum of Thin Film Nanocomposite ZnO-PVA and ZnO-PVA with addition TiO₂ concentration

Figure 4(a) shows the differences between shifted peaks for each ZnO-PVA nanocomposite with or without the addition of TiO₂ concentration. The absorption peak of the ZnO-PVA nanocomposite thin film occurred around 374 nm. The addition of TiO₂ in different concentrations of 1, 2, and 3% to the ZnO-PVA nanocomposite resulting the absorbance peak shifting to 362 and 364 nm, respectively. Due to the addition of TiO₂ concentrations, Figure 4(a) showed a shift in the excitons absorption wavelength to the blue shift. As a result, there is an increase in energy for every addition of TiO₂ to the ZnO-PVA

nanocomposite. The change in energy of the band gap is due to the depleted oxygen and crystal flaws in the titanium. The oxygen vacancies resulted in unpaired electrons associated with Ti^{3+} ions, that is initiated the creation of donor levels in the bandgap. Trivacancy imparts p-type properties to TiO_2 due to the excess of holes and generates acceptor levels in the bandgap [15]. This mechanism causes a narrowing of the band gap but increases the absorption of visible light in TiO_2 . A higher bandgap energy increase offers the ability to operate at high temperatures.

Figure 4(b) shows that the energy gap corresponding to the absorbance wavelength for the ZnO-PVA nanocomposite thin film is 3.317eV for the low band and 3.671eV for the wideband. Meanwhile, ZnO-PVA- TiO_2 nanocomposite thin films with TiO_2 concentrations of 1, 2, and 3% showed the same energy difference as ZnO-PVA wide band nanocomposites at 3.671eV. It can be said that by addition of TiO_2 may increase energy band gap of ZnO which is from 3.37 eV to 3.617eV. The change in the bandgap energy shows the amount of energy required for a particle to pass from the valence band to the conduction band.

4. Conclusion

Thin films of ZnO-PVA nanocomposites and ZnO-PVA- TiO_2 nanocomposites with three different concentrations of TiO_2 have been successfully synthesized using the spin coating method. The SEM-EDX results confirm that the ZnO-PVA nanocomposite thin film has a smoother surface than the ZnO-PVA- TiO_2 nanocomposite. This is due to the defects from the additional content in the PVA nanoparticles, causing TiO_2 to agglomerate on the ZnO-PVA nanocomposite, and EDX confirms the presence all the elemental atomic found in the nanocomposite. Then XRD succeeded in confirming the shape of the ZnO crystal structure, which is hexagonal wurtzite, with an increase in the peak intensity of $2\theta = 25.379^\circ$ and 27.433° , indicating the presence of TiO_2 and affected the average size of ZnO-PVA nanocomposite crystals to be smaller. Furthermore, based on UV-Vis result, there was a shift in the absorbance peak to the lower wavelength by adding the TiO_2 to the ZnO-PVA nanocomposite. It indicates a blue shift and increases the energy of the band gap of ZnO-PVA nanocomposite. It is concluded that the addition of TiO_2 to the ZnO-PVA nanocomposite affects the optical properties, this result potential to be applied as an optical sensor in flexible devices.

Acknowledgments

The authors would like to acknowledge Telkom University for the international matching grant of 016/PNLT3/PPM/2020 and Universiti Malaysia Kelantan under the grant of R/MTCH/A1300/00462A/004/2021/00973.

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